Name and DOI of manuscript: Sub-picosecond charge-transfer at near-zero driving force in polymer:non-fullerene acceptor blends and bilayers.
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Data acquisition: Details on the methods of data acquisition are described in the above manuscript and the corresponding S.I.

Data analysis: Details of the data analysis are described in the above manuscript and the corresponding S.I.

Figure 1
HT in J61:m-ITIC heterojunctions with different sample configurations. a. Chemical structure of m-ITIC and J61. b. TA spectra at selected time delays (see legend) recorded for the J61:m-ITIC (1:1) BHJ following excitation at 700 nm. c. m-ITIC exciton decay (top) and charge rise (bottom) dynamics for J61:m-ITIC samples under different morphological scenarios, upon selective m-ITIC excitation at 700–730 nm, obtained from the analysis of the TA data. The y-axis is expressed as a fraction of the total absorbed photon density. Symbols are the experimental data and solid lines are exponential fits obtained globally for the exciton decay and charge rise. d. sEQE and EL spectra for the J61:m-ITIC BHJ blends with 1:1 and 5:1 mass ratio. The solid and dashed black lines are fits to the EL and sEQE spectra with bi-Gaussian functions, respectively, yielding the S1 and CT energies as global parameters. e Schematic illustration of the morphology in the J61:m-ITIC bilayer and dilute (5:1 BHJ) samples.

Corresponding raw data files
TA data:
Figure 1b, 2017.4, by Yufei and Martina, lab book number 1
File name: BHJ_700nm_2_5nJ_4000sh_10sc_vis; BHJ_700nm_2_7nJ_4000sh_6sc_IR
Decomposition:
Figure 1c, 2017.5-6/2017.8, by Yufei, lab book number 1
File name: B1_th_th_700nm_3.6nj_4000sh_9sc_vis_BC;
B1_th_th_700nm_3.6nj_4500sh_15sc_IR_BC;
BHJ_700nm_2_5nJ_4000sh_10sc_vis;
BHJ_700nm_2_7nJ_4000sh_6sc_IR;
J61MITIC_730nm_30nJ_4000sh_10sc;
J61MITIC_730nm_30nJ_MA_NIR_4000sh_6sc;
EQE and EL data:
Figure 1d, 2018.9, by Johannes and Jonas

Figure 2
Comparison of the ET and HT processes in J61:m-ITIC. a. m-ITIC and J61 exciton decay and charge rise dynamics in the J61:m-ITIC (1:1 BHJ) sample under 700 and 480 nm excitation obtained from the analysis of the experimental TA data (top), and corresponding dynamics simulated by kinetic modeling (bottom). b. Schematic representation of the processes used in the kinetic model within the phase morphology of the blend, which comprises m- ITIC-rich domains (orange), neat ordered polymer domains (green) and intermixed donor–acceptor regions. c. Jablonski diagram and time constants for the processes described by the kinetic model: i. 100% and 28% of photons are directly absorbed by m-ITIC at 700 and 480 nm, respectively, which then undergoes intrinsic and diffusion-mediated HT; ii. At 480 nm, J61

excitons generated within 1.9 nm of a m-ITIC interface undergo ultrafast ET; iii. J61 excitons generated further from an interface undergo diffusion-mediated ET in competition with EET followed by interfacial intrinsic HT, which is predominant due to a shallower distance dependence of EET. Note that all multiphasic processes are approximated with average time constants, leading to some differences with the experimental data. d. Excitation profiles (percentage of total incident photons absorbed per nanometer, calculated by TMM) for the bilayer sample at both excitation wavelengths.

Corresponding raw data files
Decomposition:
Figure 2a, 2017.5-6, by Yufei and Martina, lab book number 1
File name: BHJ_480nm_14.5nJ_4000sh_4sc_vis; BHJ_480nm_14.5nJ_4500sh_5sc_IR_FC; BHJ_700nm_2_5nJ_4000sh_10sc_vis; BHJ_700nm_2_7nJ_4000sh_6sc_IR
TMM:
Figure 2d, 2019.9, by Philipp

Figure 3
Driving force dependent sub-picosecond HT in polymer:m-ITIC blends. a. sEQE spectra for the polymer:m-ITIC 5:1 blends and neat m-ITIC. The curves are shifted to always have the m-ITIC S1 energy (from a bi-Gaussian fit of the sEQE and EL data) at 0 eV for better comparison. At the bottom, a schematic illustration of the driving forces for HT in polymer:m-ITIC 5:1 BHJ samples is shown. b. m-ITIC exciton decay (top) and charge rise (bottom) dynamics for polymer:m-ITIC 5:1 BHJ samples, upon selective m-ITIC excitation at 730 nm, obtained from the analysis of the TA data. The y-axis is expressed as a fraction of the total absorbed photon density. Symbols are the experimental data and solid lines are exponential fits obtained globally for the exciton decay and charge rise.

Corresponding raw data files
EQE:
Figure 3a, 2018.9, by Johannes and Jonas
Decomposition:
Figure 3b, 2018.8/2019.1, by Yufei and Gareth, lab book number 2 and 3
File name: 5to1P3HTBHJ_730nm_77nj_MAG_4000sh_6sc_IR; 5to1PBTTTBHJ730nm_MA_70nj_4000sh_6sc; 5too1PBTTTBHJ730_70nj_4000sh_12sc; BHJ_P3HT_730nm_77nJ_4000sh_12sc; J61MITIC_730nm_30nJ_4000sh_10sc; J61MITIC_730nm_30nJ_MA_NIR_4000sh_6sc; TA_PCDTBT5to1_730nm_10nj_IR_4000sh_35sc; TA_PCDTBT5to1_730nm_10nj_VIS;

Figure 4
Relationship between the driving force and the HT and ET rates. a. The charge-transfer rate (inverse of the first time constant obtained from the analysis of the TA dynamics) for ET and HT in different polymer:m-ITIC BHJ blends is plotted against the driving force (obtained from the sEQE and EL spectra). The red solid line is a guide for the eye to show the trend in HT rate, while the black curves represents the CT rate predicted from semiclassical Marcus–Levich–Jortner theory (with transfer integral JDA = 14– 32 meV, Huang−Rhys parameter S = 1 and outer re-organization energy λo = 0.15 eV). b. LUMO–LUMO transfer integral for ET and HOMO–HOMO transfer integral for HT in a J61:m-ITIC complex as a function of the

donor:acceptor (D:A) distance. The geometry as obtained by DFT calculations (at 4.5 Å) is depicted in the inset.

MLJ plot:
Figure 4a, 2017.5/2017.8/2018.8/2019.1, by Yufei, Martina, Gareth, lab book number 1, 2, 3

DFT transfer integral:
Figure 4b, 2019.10, by Frank

Selected raw data and data in the SI is available from the authors upon request:
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